THE PREPARATION OF ORGANOMETALLIC AND ORGANOMETALLOIDAL COMPOUNDS BY THE DIAZOALKANE METHOD

DIETMAR SEYFERTH[1]

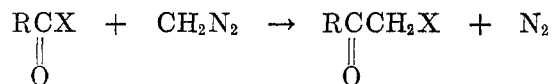*Departmnt of Chemistry, Harvard University, Cambridge, Massachusetts*

CONTENTS

I. INTRODUCTION

Diazomethane, since its discovery by von Pechmann in 1894 (31), has proved exceedingly useful in preparative and theoretical organic chemistry and has been the subject of a number of reviews (1, 3, 5, 17, 20, 23, 44, 46). The majority of the examples of those reactions of diazomethane and its higher homologs and of substituted diazomethanes which lead to the formation of a carbon–metal bond have only been described within the last few years and have not been discussed in detail in any of the reviews cited above. It is the object of this review to point out the great usefulness of diazoalkanes in the preparation and study of organometallic and organometalloidal compounds.

Among the first reactions of diazomethane described in the literature were

When two equivalents were added, a quantitative yield of bis(chloromethyl)-mercury was obtained:

$$HgCl_2 + 2CH_2N_2 \rightarrow (ClCH_2)_2Hg + 2N_2$$
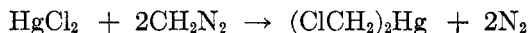
Treatment of mercuric chloride with diphenyldiazomethane, $(C_6H_5)_2CN_2$, under the same conditions gave (diphenylchloromethyl)mercuric chloride, an amorphous white solid that was unstable toward moisture. Mercuric chloride was reduced to metallic mercury by the action of diazomethane when an alcoholic solvent was used as the reaction medium instead of ether (28).

In contrast to mercuric chloride, mercuric iodide did not react smoothly with diazomethane (21). The action of one or two equivalents of diazomethane on mercuric iodide yielded only a small amount of bis(iodomethyl)mercury and, in addition, a large amount of gummy material was formed. This difference in the course of the reaction of the two mercuric halides was attributed by the investigators to the much greater tendency of mercuric iodide to form internal complexes of the type $(HgI_2)_x$.

p-Tolylmercuric chloride apparently formed p-tolyl(chloromethyl)mercury when treated with diazomethane in ether solution, but this immediately underwent disproportionation and di-p-tolylmercury precipitated, while bis(chloromethyl)mercury remained in solution:

$$p\text{-}CH_3C_6H_4HgCl + CH_2N_2 \rightarrow p\text{-}CH_3C_6H_4HgCH_2Cl + N_2$$

$$2p\text{-}CH_3C_6H_4HgCH_2Cl \rightarrow (p\text{-}CH_3C_6H_4)_2Hg + (ClCH_2)_2Hg$$
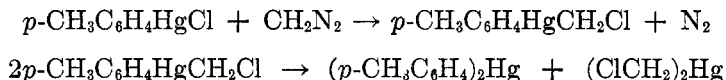
Phenyl(chloromethyl)mercury was obtained in a similar manner as a liquid that slowly deposited crystals of diphenylmercury, while benzyl(chloromethyl)-mercury, an oil obtained by treating benzylmercuric chloride with ethereal diazomethane, proved to be quite stable toward disproportionation (21).

Bromomethylmercuric bromide was obtained in low yield by the action of diazomethane either on mercuric bromide or on the basic mercuric bromide-ethylene complex (19). The course of the latter reaction was complicated, since metallic mercury and formaldehyde were obtained as by-products:

$$C_2H_4 \cdot Hg(OH)Br + CH_2N_2 \rightarrow C_2H_4 \cdot Hg(OH)CH_2Br + N_2$$

$$C_2H_4 \cdot Hg(OH)CH_2Br \rightarrow C_2H_4 + HOHgCH_2Br$$

$$HOHgCH_2Br \rightarrow Hg + HBr + HCHO$$

$$HOHgCH_2Br + HBr \rightarrow BrCH_2HgBr + H_2O$$
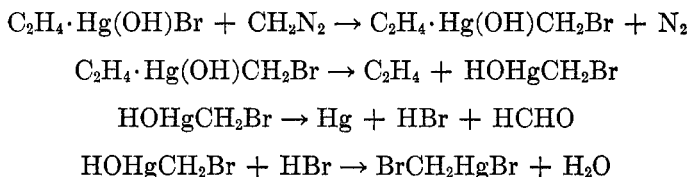
The intermediate $C_2H_4 \cdot Hg(OH)CH_2Br$ seemed to be relatively stable in solution, since ethylene was not given off until the ether used as solvent had been removed. It could be isolated as an oil, stable below 0°C. Bis(bromomethyl)-mercury was obtained in quantitative yield by the action of a large excess of diazomethane on mercuric bromide (19).

Diazomethane may be prepared *in situ* in the presence of mercuric salts to yield methylenated products (29). Thus, isoamyl nitrite and mercuric chloride, upon the addition of methylamine hydrochloride in the presence of copper powder in methyl alcohol solution, gave chloromethylmercuric chloride in low yield. This reaction is not observed in the absence of copper powder.

The reaction of mercuric chloride with ethyl diazoacetate, $N_2CHCOOC_2H_5$, is more complex, but also gives a chloromethyl derivative (29). The acidic α-hydrogen atom of the ester is simultaneously mercurated, while the liberated hydrogen chloride attacks another molecule of ethyl diazoacetate, forming ethyl chloroacetate:

$$4N_2CHCOOC_2H_5 \;+\; 3HgCl_2 \;\rightarrow\; Hg\left[\begin{array}{c} Cl \\ | \\ -CCOOC_2H_5 \\ | \\ HgCl \end{array}\right]_2 \;+\;$$

$$4N_2 \;+\; 2ClCH_2COOC_2H_5$$
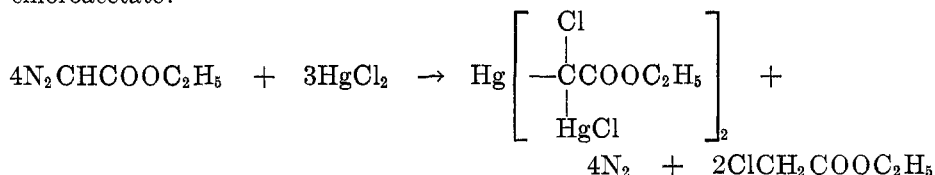
The mercuration of ethyl diazoacetate by mercuric oxide had been previously observed by Buchner (9):

$$2N_2CHCOOC_2H_5 + HgO \rightarrow Hg[C(N_2)COOC_2H_5]_2 + H_2O$$
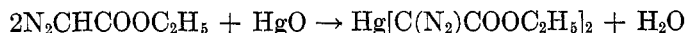
and it was later shown (29) that the reaction of the mercurated product with mercuric chloride does not result in the formation of a chloromethyl derivative of mercury.

Recently Pfeiffer and coworkers discovered that arylmercury salts of organic acids undergo the methylenation reaction as well, but give only 15–20 per cent yields (32, 33):

$$C_6H_5HgOOCC_6H_5 + CH_2N_2 \rightarrow C_6H_5HgCH_2OOCC_6H_5 + N_2$$
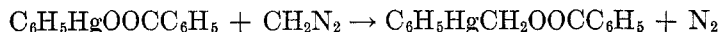
These are the only examples found of the reaction of a metal–oxygen bond with diazomethane. The products are not stable in solution; they tend to undergo a disproportionation reaction similar to that given by the unsymmetrical chloromethyl compounds described above.

$$2ArHgCH_2OOCAr' \rightarrow Ar_2Hg + Hg(CH_2OOCAr')_2$$

Mercuric cyanide, diphenylmercury, and di-*p*-tolylmercury did not react with diazomethane (21).

2. Zinc

Zinc chloride has been effectively used as a catalyst in the methylation of butanol with diazomethane (28), but no organozinc product was reported. The reaction of zinc chloride with diazomethane in ether solution has been studied (11). No organozinc compound was isolated, but the products of the reaction, zinc oxide, *n*-butane, and 1,2-dichloroethane, were presented as proof for the transient existence of unstable bis(chloromethyl)zinc:

$$ZnCl_2 + 2CH_2N_2 \rightarrow Zn(CH_2Cl)_2 + 2N_2$$

$$Zn(CH_2Cl)_2 + (C_2H_5)_2O \rightarrow ZnO + ClCH_2CH_2Cl + C_4H_{10}$$
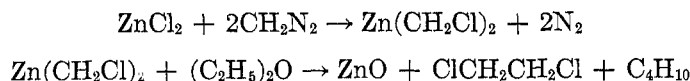
3. Magnesium

Grignard reagents do not undergo the methylenation reaction. In all cases products are obtained that contain nitrogen, and it seems that diazomethane reacts as if the predominant contribution were being made by the resonance form $H_2C=\overset{\oplus}{N}=\overset{\ominus}{N}$. Thus Zerner (62), in his study of the reaction of diazomethane and ethyl diazoacetate with Grignard reagents, found evidence to indicate that hydrazones were formed:

$$\begin{array}{c} H \\ \diagdown \\ C=\overset{\oplus}{N}=\overset{\ominus}{\underset{\cdot\cdot}{N}}: \\ \diagup \\ H \end{array} \xrightarrow{\ \ RMgX\ \ } \xrightarrow{\ \ H_2O\ \ } \begin{array}{c} H \qquad\qquad R \\ \diagdown \qquad\quad \diagup \\ C=N-N \\ \diagup \qquad\quad \diagdown \\ H \qquad\qquad H \end{array}$$
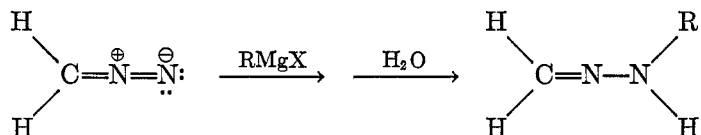
A more detailed study by later investigators (13) confirmed that the reaction of diphenyldiazomethane with Grignard reagents gave hydrazones. On the other hand, the reaction of diazomethane with a large excess of phenylmagnesium bromide yielded benzylphenylhydrazine, presumably by the following sequence of reactions:

$$CH_2N_2 \ + \ C_6H_5MgBr \ \rightarrow \ H_2C=NN\diagup^{C_6H_5}_{\diagdown MgBr}$$

$$CH_2=NN\diagup^{C_6H_5}_{\diagdown MgBr} \ + \ C_6H_5MgBr \ \rightarrow \ H_2C\underset{\underset{C_6H_5}{|}}{\overset{\overset{MgBr}{|}}{-}}N-N\diagup^{C_6H_5}_{\diagdown MgBr}$$

$$H_2C\underset{\underset{C_6H_5}{|}}{\overset{\overset{MgBr}{|}}{-}}N-N\diagup^{C_6H_5}_{\diagdown MgBr} \ + \ 2H_2O \ \rightarrow \ H_2C\underset{\underset{C_6H_5}{|}}{N}HNHC_6H_5 \ + \ 2Mg(OH)Br$$
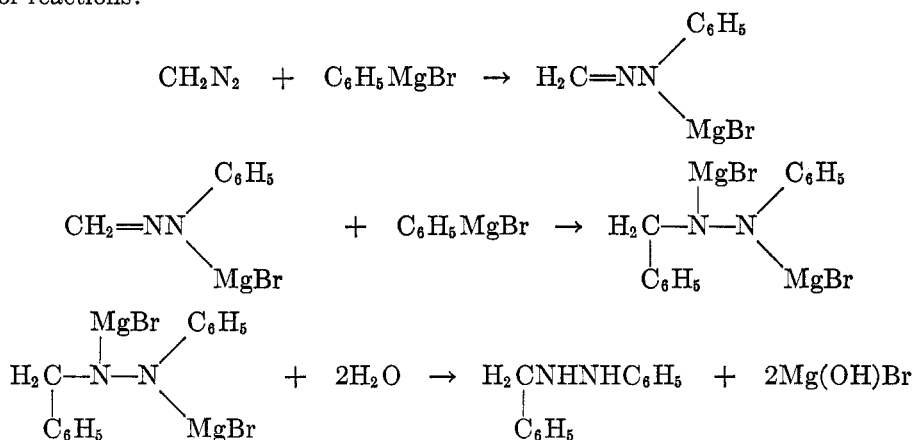
Reduction seemed to occur when diazomethane was treated with alkyl Grignard reagents, since methylhydrazines were obtained as products:

$$CH_2N_2 \xrightarrow{\ C_6H_5CH_2MgCl\ } \xrightarrow{\ H_2O\ } CH_3NHNHCH_2C_6H_5$$

$$CH_2N_2 \xrightarrow{\ n\text{-}C_4H_9MgBr\ } \xrightarrow{\ H_2O\ } CH_3NHNHC_4H_9\text{-}n$$
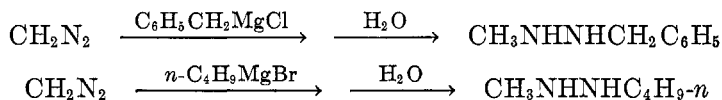
No definite products were obtained from the reaction of ethylmagnesium iodide, methylmagnesium iodide, or methylmagnesium bromide with diazomethane. Only decomposition seemed to occur.

B. ELEMENTS OF PERIODIC GROUP III

1. Boron

No halomethyl derivatives of boron were obtained by treatment of boron trichloride, boron tribromide, or phenylboron dichloride with diazomethane,

even at −75°C. (54). All boron compounds merely catalyzed the decomposition of diazomethane to polymethylene. In this respect boron seems to occupy a unique position with respect to the behavior of halides of the other B subgroup metals toward diazomethane, although possibly the same behavior may be expected with the aluminum halides, whose reaction with diazomethane has not yet been examined. Meerwein (27) had previously reported that a variety of boron compounds (trialkylborines, trialkyl borates, the boron halides, pyroboric acetate) decompose diazomethane catalytically at 17°C. in solution to give an almost quantitative yield of polymethylene. Other workers have used catalytic amounts of trimethyl borate (10) and boron trifluoride (24) to prepare polymethylenes of very high molecular weight. These reactions will be discussed in greater detail in the section devoted to the mechanism of the methylenation reaction.

2. Thallium

Thallium trichloride was found to undergo the methylenation reaction (54). Thus bis(chloromethyl)thallium chloride, an unstable, explosive solid, was obtained from the reaction of thallium trichloride with diazomethane. Treatment of thallium trichloride with diazoethane in ether solution yielded $(CH_3CHClTlCl)_2O$, as well as a small amount of $3TlCl·TlCl_3$. The former product probably resulted from the partial hydrolysis of the α-chloroethylthallium chloride originally formed, due to the incomplete drying of the ether used as solvent.

C. ELEMENTS OF PERIODIC GROUP IV

1. Silicon

Silicon tetrachloride and silicon tetrabromide were methylenated if the reactions were conducted at −55°C. to −45°C. (56, 60). At room temperature only catalytic decomposition, sometimes explosive, of the diazomethane occurred. Silicon tetrafluoride, on the other hand, did not react to form a fluoromethylsilicon derivative even at very low temperatures; only the formation of polymethylene was observed. The introduction of one methylene group into silicon tetrachloride to form chloromethyltrichlorosilane proceeds readily, and yields as high as 60 per cent have been reported (42, 56). Yields of 73 per cent have been reported for the methylenation of trichlorosilane (42). The introduction of a second and of subsequent methylene groups took place with increasing difficulty (56). Thus a yield of only 30–35 per cent of bis(chloromethyl)dichlorosilane was obtained on treating chloromethyltrichlorosilane with diazomethane at −35°C., and the yield of tris(chloromethyl)chlorosilane was only 10–15 per cent even when a catalyst was used. No tetrakis(chloromethyl)silane could be prepared by the methylenation reaction. Unsubstituted alkylchlorosilanes, such as methyltrichlorosilane, were methylenated with even greater difficulty; chloromethylmethyldichlorosilane was obtained in 13 per cent yield. In the latter reaction and in those where more than one methylene group was to be introduced, copper bronze powder or powdered anhydrous copper sulfate seemed

to function as catalyst (56). Triorganochlorosilanes, such as trimethylchlorosilane (42), triethylchlorosilane (56), and triphenylchlorosilane (42), were not methylenated at all, and only the unchanged silanes and small amounts of their hydrolysis products were recovered. No reaction occurred, even at room temperature, between diazomethane and tetraethoxysilane (42).

Diazomethane reacted less energetically and, it is claimed, at a slower rate with silicon tetrabromide than with silicon tetrachloride, but the ease with which methylene groups were introduced increased. The yields of bis(bromomethyl)dibromosilane (55 per cent) and of tris(bromomethyl)bromosilane (40 per cent) obtained were much higher than those of the corresponding chloromethylsilanes, even in the absence of a catalyst. Furthermore, methylenation gave tetrakis(bromomethyl)silane (which decomposed on attempted distillation), but, as has been mentioned before, no tetrakis(chloromethyl)silane (56, 60).

Diazoethane reacted with silicon tetrachloride, but more vigorously than diazomethane, and α-chloroethylchlorosilanes resulted (56, 60).

2. Germanium

The reaction of diazomethane with germanium tetrachloride, methylgermanium trichloride, and dimethylgermanium dichloride has been examined (42). Treatment of germanium tetrachloride with one equivalent of diazomethane in ether solution at −60°C. to −70°C. in the presence of a small amount of copper powder resulted in a 93.7 per cent yield of chloromethylgermanium trichloride (based on the unrecovered germanium tetrachloride) and in a very small yield of bis(chloromethyl)germanium dichloride. Similarly, treatment of methylgermanium trichloride with diazomethane (one equivalent) gave chloromethylmethylgermanium dichloride in 78 per cent yield. The reaction of methylgermanium trichloride with two equivalents of diazomethane under the same conditions yielded chloromethylmethylgermanium dichloride (33.5 per cent) and methylbis(chloromethyl)germanium chloride (20.5 per cent). Dimethylgermanium dichloride was not methylenated at −60°C. or at 0°C. in the presence of copper powder. From these results it is apparent that the germanium chlorides undergo the methylenation reaction much more readily than do the chlorosilanes.

3. Tin

The reaction of diazoalkanes with tin halides has been the subject of extensive study. No tin–carbon bonds were formed by treatment of tin tetrachloride with ethyl diazoacetate in petroleum ether solution (30). A product,

$$[N_2C\!\!=\!\!C(OC_2H_5)O]_2SnCl_2$$

which began to decompose at room temperature a few minutes after its formation, was obtained, as well as nitrogen and ethyl chloroacetate. The latter products resulted from the reaction of hydrogen chloride, formed in the primary step, with the diazoacetic ester.

Brief mention has been made of unpublished work by Nesmeyanov and

Woronzova on the action of diazomethane on tin tetrachloride (30). The results cited show that the tin tetrachloride was reduced under the conditions used:

$$CH_2N_2 + SnCl_4 \rightarrow CH_2Cl_2 + N_2 + SnCl_2$$

More recently the reaction of diazoalkanes with tin tetrachloride and other tin halides has been investigated by Yakubovich and his coworkers (59, 60). The action of diazomethane on stannous chloride suspended in ether yielded a partially substituted derivative of tetravalent tin, believed to be

$$Cl_2Sn\overset{\displaystyle CH_2-SnCl_2}{\underset{\displaystyle CH_2-SnCl_2}{}}O \cdot (C_2H_5)_2O$$
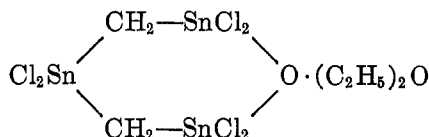
In benzene solution high-molecular-weight products of the type

$$\left[-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Sn}}-CH_2- \right]_n$$
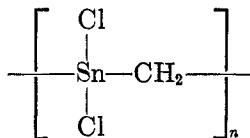
were formed, presumably by polymerization of the initial addition product:

$$\ominus :\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Sn}}-\overset{\oplus}{C}H_2$$
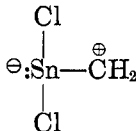
Methylenations of tin tetrachloride were carried out at 0–5°C. in benzene solution. Ether could not be used as a solvent, since tin tetrachloride forms the difficultly soluble $SnCl_4 \cdot 2(C_2H_5)_2O$. A mixture of chloromethyl derivatives, $ClCH_2SnCl_3$, $(ClCH_2)_2SnCl_2$, and $(ClCH_2)_3SnCl$, was formed in 30–40 per cent yield. Separation of the products was accomplished only with difficulty. This distribution of products was obtained even if tin tetrachloride was used in an excess of 50 per cent over the amount required to form chloromethyltin trichloride. By treating tin tetrachloride with an excess of diazomethane (6 moles of diazomethane to 1 mole of tin tetrachloride) in benzene solution tetrakis-(chloromethyl)tin could be prepared in 57 per cent yield. The reaction of tin tetrabromide with diazomethane proceeded even more readily and gave better yields of the four possible bromomethyl derivatives. Tin tetrafluoride did not undergo the methylenation reaction.

Diazoethane acts on tin tetrachloride in a similar manner to diazomethane. In this case, however, even with a 2:1 molar ratio of tin tetrachloride to diazo-ethane, bis(α-chloroethyl)tin dichloride is the main product. Smaller amounts of the mono- and trisubstituted products are obtained as well. The disubstituted compound was also the main product in the reaction of diazobutane with tin tetrachloride.

Mixed α-chloroalkyl derivatives of tin have also been prepared *via* the diazo method by the same investigators (59). Thus, bis(chloromethyl)bis(α-chloroethyl)tin was obtained in 23.4 per cent yield by treating bis(chloromethyl)tin dichloride with diazoethane.

The reaction of diazomethane with organotin halides has also been examined (43). Dimethyltin dichloride, dimethyltin dibromide, and dimethyltin diiodide, when treated with slightly more than one equivalent of diazomethane in ether solution at 0–5°C. (vigorous stirring during the addition of the diazomethane solution to the dimethyltin dihalide solution), gave the corresponding halomethyldimethyltin halides in yields of 70–80, 73, and 78 per cent, respectively. These products, heavy colorless liquids, were powerful lachrymators and vesicants. *n*-Butyl(chloromethyl)tin chlorides were similarly prepared.

It was impossible to isolate bromomethyldiphenyltin bromide from the reaction of diphenyltin dibromide with diazomethane. The product and the starting material could not be separated by fractional distillation at reduced pressure. However, treatment of the distillate with a large excess of neutral aqueous-alcoholic potassium fluoride solution precipitated bromomethyldiphenyltin fluoride (43).

The introduction of a methylene group into triorganotin halides could not be detected in ether solution at 5–10°C. (43). When triphenyltin chloride, triphenyltin iodide, or tri-*n*-butyltin chloride was treated with an excess of diazomethane under these conditions, only the starting materials were recovered.

It is also interesting to note that very recently a gasometric method for the determination of the concentration of a diaryldiazomethane solution was described (40), which involved treatment of an aliquot of the solution with tin tetrachloride pentahydrate and measurement of the nitrogen evolved in a eudiometer.

4. Lead (60, 61)

The methylenation of inorganic lead compounds was unsuccessful. Lead tetrachloride, even at −15°C. to −20°C., chlorinated the solvent, or, in carbon tetrachloride, decomposed spontaneously into lead dichloride and chlorine. A stable lead tetrachloride derivative, ammonium hexachloroplumbate, did not react because of its insolubility in all suitable solvents. For the same reason lead dichloride could not be methylenated. Lead tetraacetate, which is soluble in benzene, reacted with diazomethane with evolution of nitrogen, but only reduction products were formed:

$$(CH_3COO)_4Pb + CH_2N_2 \rightarrow (CH_3COO)_2Pb + (CH_3COO)_2CH_2 + N_2$$

It was found, however, that alkyllead chlorides, which are somewhat soluble in ether, could be methylenated in low yield. A copper bronze catalyst and temperatures of 10–15°C. were required to effect the reaction. Thus, the reaction of triethyllead chloride with diazomethane under these conditions gave a mixture of chloromethyltriethyllead and tetraethyllead, from which the chloromethyl derivative could be isolated by repeated vacuum fractionation. A yield of 73

per cent was obtained. Bis(chloromethyl)diethyllead, prepared by the reaction of diethyllead dichloride with diazomethane, was a poorly stable compound which decomposed with separation of a precipitate even in the dark. Triethyllead chloride, when treated with diazoethane as described above, gave α-chloro-ethyltriethyllead, which, however, could not be isolated owing to its instability with respect to disproportionation into tetraethyllead and lead dichloride when the ether solvent was removed at −15°C.

D. ELEMENTS OF PERIODIC GROUP V

1. Nitrogen

Only acid halides of nitrogen have been treated with diazoalkanes, and only the reactions with nitryl chloride gave α-chloroalkyl derivatives (52). Thus treatment of nitryl chloride, NO_2Cl, with diazomethane in ice-cold ether solution caused evolution of nitrogen, and chloronitromethane, $ClCH_2NO_2$, was obtained. Ethyl diazoacetate similarly yielded chloronitromethane and a small amount of ethyl chloronitroacetate:

$$NO_2Cl + N_2CHCOOC_2H_5 \rightarrow N_2 + ClCH_2NO_2 + O_2NCHClCOOC_2H_5$$

It has been mentioned (48) that nitrosyl chloride, NOCl, reacts vigorously with diphenyldiazomethane, but no products were isolated. The action of nitrosyl chloride on ethyl diazoacetate yielded no methylenated products (45).

2. Phosphorus

In early work on the formation of phosphazines by the reaction of diazoalkanes with triorganophosphines (51),

$$Ar_2CN_2 + R_3P \rightarrow R_3P{=}N{-}N{=}CAr_2$$

it was noted that phosphorus trichloride and phenyldichlorophosphine did not add to the diazoalkanes in this manner. No mention was made, however, of the possible formation of carbon–phosphorus bonds.

The treatment of phosphorus trichloride with diazomethane in ether solution at room temperature was studied by Pletz (34), but only tarry products were obtained from the vigorous reaction. Similarly, amyl nitrite, methylamine hydrochloride, and phosphorus trichloride in ether solution (i.e., preparation of diazomethane *in situ*) yielded a reddish-yellow tar.

Yakubovich and his coworkers achieved successful methylenation of phosphorus halides by using low temperatures (55, 57). Thus, phosphorus trichloride reacted with diazomethane in ether solution at −60°C. to −50°C. to give a 40 per cent yield of chloromethyldichlorophosphine. Diazoethane and diazobutane reacted similarly. Bromomethyldibromophosphine was obtained in 50 per cent yield when the ratio of phosphorus tribromide to diazomethane was 3:1. If the ratio was decreased to 2:1 or 1:1, the amount of solid by-product (which always formed in the reactions of phosphorus trihalide with diazomethane) increased and the yield of halomethyl derivative dropped to 15–20

per cent. More than one methylene group could not be introduced into trivalent phosphorus halides; only "more complex solid products" were obtained when further substitution was attempted. However, di- and trisubstitution could be effected when phosphorus pentachloride was treated with diazomethane. The action of an excess of diazomethane on phosphorus pentachloride in ether solution at $-40°C$. gave tris(chloromethyl)phosphine oxide, $(ClCH_2)_3PO$, in 50–70 per cent yield. The reaction of diazoethane with phosphorus pentachloride (5:1 molar ratio) under the same conditions, followed by hydrolysis of the product, gave bis(α-chloroethyl)phosphinic acid, $(CH_3CHCl)_2P(O)OH$. It proved impossible, however, to methylenate phosphorus oxychloride or phosphorus oxybromide, even when copper bronze powder or powdered anhydrous copper sulfate was used as catalyst.

In all the reactions of phosphorus halides with diazoalkanes by-products were isolated that arose from the reaction of products of the partial hydrolysis of the starting phosphorus halide with the diazoalkane. Thus the preparation of chloromethyldichlorophosphine yielded a small amount of CH_3OPCl_2 as well, which was formed by the following reactions:

$$PCl_3 + H_2O \rightarrow HOPCl_2 + HCl$$

$$CH_2N_2 + HOPCl_2 \rightarrow CH_3OPCl_2 + N_2$$
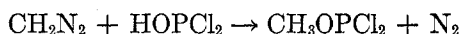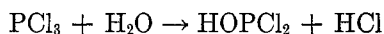
One example in which the phosphorus–fluorine link enters into a methylenation reaction has been described (37). Di-sec-butyl fluorophosphonate, (sec-$C_4H_9O)_2PF$, reacted at $0°C$. with diazomethane in ether solution to give di-sec-butyl(fluoromethyl) phosphonate, (sec-$C_4H_9O)_2PCH_2F$.

3. Arsenic

α-Chloroalkyl arsenic derivatives were readily formed in the reaction of diazoalkanes with arsenic trichloride in ether solution at 0–$5°C$. (8, 57, 58). In contrast to the phosphorus trihalides, where only monosubstitution could be realized, the reaction of diazomethane with arsenic trichloride gave bis(chloromethyl)chloroarsine as well as chloromethyldichloroarsine (8). Diazoethane methylenated arsenic trichloride so readily that even if the molar ratio of diazoethane to arsenic trichloride was reduced to 1:1.5, only the formation of bis(α-chloroethyl)chloroarsine (40 per cent yield) occurred (57, 58). Complete alkylation to tris(α-chloroethyl)arsine occurred only with difficulty (26 per cent yield) when arsenic trichloride was treated with an excess of diazoethane.

The reaction of diazomethane with diphenylchloroarsine in ether at $0°C$. took an unusual course (14). Instead of the expected chloromethyldiphenylarsine, methylenebis(diphenylarsine) monoxide, $(C_6H_5)_2As(O)CH_2As(C_6H_5)_2$, was obtained. It seemed likely to the investigators that the arsine oxide was a direct product of the main reaction and did not arise by subsequent oxidation of methylenebis(diphenylarsine), because the latter did not undergo oxidation under the conditions employed. It was claimed that a trace of water in the

diazomethane solution hydrolyzed the diphenylchloroarsine, and that the reaction then took the following course:

$$2(C_6H_5)_2AsCl + H_2O \rightarrow (C_6H_5)_2AsOAs(C_6H_5)_2 + 2HCl$$

$$(C_6H_5)_2AsOAs(C_6H_5)_2 \; + \; \overset{\oplus}{C}H_2-N=\overset{\ominus}{N} \; \rightarrow \; (C_6H_5)_2\overset{\oplus}{As}-O-As(C_6H_5)_2$$
$$\overset{|}{C}H_2-N=N^{\ominus}$$

$$(C_6H_5)_2AsCH_2^{\ominus} \quad \overset{\oplus}{As}(C_6H_5)_2 \quad \rightarrow \quad (C_6H_5)_2As(O)CH_2As(C_6H_5)_2$$
$$\overset{\|}{O}$$
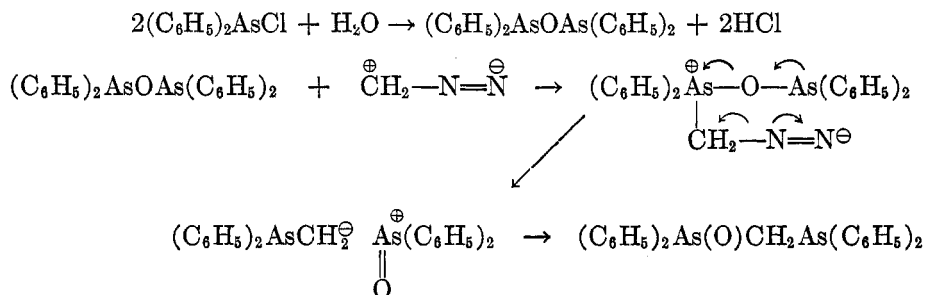
This hypothesis was, unfortunately, not tested by treating the readily available bis(diphenylarsenic) oxide with diazomethane.

4. Antimony (57, 58)

Diazomethane was found to react with antimony trichloride in benzene solution at 3–5°C., forming chloromethyldichlorostibine in 54 per cent yield if an excess of antimony trichloride was used. Tris(chloromethyl)stibine was obtained in 35.2 per cent yield if an excess of diazomethane was used. Similarly bis(α-chloroethyl)chlorostibine was formed in 52 per cent yield by the reaction of diazoethane with antimony trichloride in 2:1 molar ratio. Antimony pentachloride, however, underwent reduction on treatment with diazomethane:

$$SbCl_5 + CH_2N_2 \rightarrow SbCl_3 + CH_2Cl_2 + N_2$$
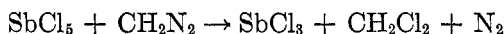
5. Bismuth (57, 58)

Exceedingly unstable (spontaneous combustion in air) chloromethylbismuth oxide, $ClCH_2BiO$, a light silver-green powder, was formed in good yield by the action of diazomethane on bismuth trichloride in ether solution at 0–3°C. Even the most careful drying of the solvent did not help in the attempted isolation of the intermediate chloromethylbismuth dichloride. This compound could, however, be prepared in impure form by the action of concentrated hydrochloric acid on the oxide.

E. ELEMENTS OF PERIODIC GROUP VI

1. Sulfur

Sulfenyl halides reacted with diazoalkanes in the usual manner to give halomethyl derivatives (38, 39). Thus, for example, o-nitrophenylsulfenyl chloride, when treated with diphenyldiazomethane in ether solution at 0°C., gave o-nitrophenyl diphenylchloromethyl sulfide in 85.4 per cent yield, while o-nitrophenylsulfenyl bromide yielded o-nitrophenyl diphenylbromomethyl sulfide on treatment with diphenyldiazomethane.

In addition, some acid halides of sulfur have been treated with diazomethane and substituted diazomethanes, but the results are at first sight somewhat

confusing. Methylenation and chlorination seem to be competing reactions, and a diazosulfoxide has been claimed as well.

Thionyl chloride, $SOCl_2$, was methylenated by diazomethane at temperatures below 5°C. in ether solution, and bis(chloromethyl) sulfoxide, $(ClCH_2)_2SO$, was obtained (37). On the other hand, with diphenyldiazomethane (48) and 9-fluorenyldiazomethane (49) thionyl chloride reacted only slowly in petroleum ether solution, and the products isolated were diphenyldichloromethane and 9,9-dichlorofluorene, respectively. It has been suggested (48) that a methylenated product is first formed and that this then decomposes:

$$(C_6H_5)_2CN_2 \; + \; SOCl_2 \; \rightarrow \; (C_6H_5)_2CCl \cdot SOCl \; + \; N_2$$
$$\downarrow$$
$$(C_6H_5)_2CCl_2 \; + \; SO$$
$$\downarrow$$
$$\tfrac{1}{2}SO_2 \; + \; \tfrac{1}{2}S$$
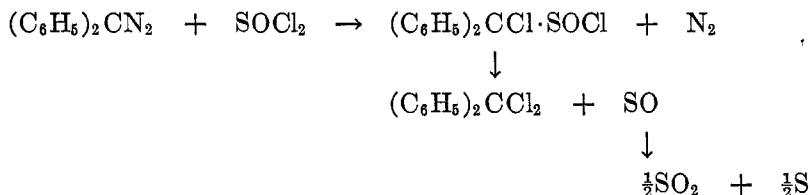
It has been reported (2) that p-toluenesulfinyl chloride reacted vigorously with diazomethane to give p-tolyl chloromethyl sulfoxide, p-$CH_3C_6H_4S(O)CH_2Cl$, as the main product. In addition, the formation of a diazosulfoxide as a by-product was claimed. In contrast, p-toluenesulfonyl chloride did not react with diazomethane (4). No evolution of nitrogen was observed. Methanesulfonyl chloride was equally unreactive at 0°C., but at 15–20°C. a reaction occurred. However, no sulfur–carbon bonds were formed, and a polymethylene was the sole product.

Sulfuryl chloride, SO_2Cl_2, acted solely as a chlorinating agent. The action of diphenyldiazomethane (48) and 9-fluorenyldiazomethane (49) on sulfuryl chloride was very vigorous; nitrogen and sulfur dioxide were evolved and the corresponding diaryldichloromethanes were formed:

$$(C_6H_5)_2CN_2 + SO_2Cl_2 \rightarrow (C_6H_5)_2CCl_2 + N_2 + SO_2$$
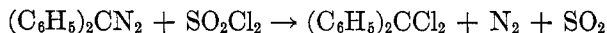
III. THE MECHANISM OF THE METHYLENATION REACTION

No single structure can satisfactorily describe the diazomethane molecule; it must be represented as a resonance hybrid of several charge-separated forms.
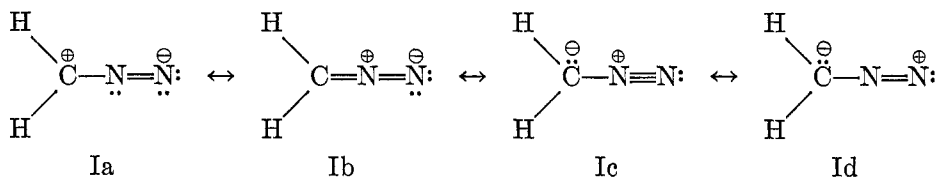
That the diazomethane molecule is linear rather than cyclic (II),
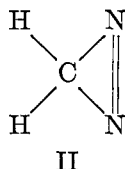
as it was first formulated, was proven by electron diffraction (7) and infrared absorption studies (15, 35).

Hellerman and Newman (21) postulated a polar mechanism for the methylenation reaction in which nucleophilic attack of the diazomethane molecule (the contribution of the carbanionic form Ic being the most important) on the mercuric halides resulted in an ionic complex, III, which subsequently lost nitrogen to yield the halomethyl derivative:

$$\underset{\underset{\text{Cl}}{|}}{\overset{\overset{\text{R}}{|}}{\text{Hg}}} \;+\; :\overset{\ominus}{\text{CH}}_2\overset{\oplus}{\text{N}}{\equiv}\text{N} \;\rightarrow\; \left[\underset{\text{HgCH}_2\text{N}{\equiv}\text{N}}{\overset{\overset{\text{R}}{|}}{}}\right]^{\oplus} \text{Cl}^{\ominus} \;\rightarrow\;$$

III

$$\text{N}_2 \;+\; [\text{RHgCH}_2]^{\oplus}\text{Cl}^{\ominus} \;\rightarrow\; \text{RHgCH}_2\text{Cl}$$
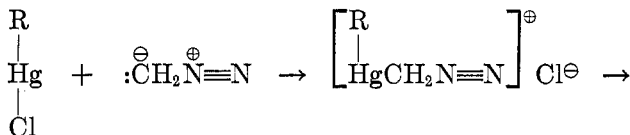
Pfeiffer and coworkers (33) favored a similar mechanism for the reaction of diazomethane with organomercury salts of aromatic acids:

$$[\text{RCOO}]^-[\text{HgAr}]^{\oplus} \;\rightarrow\; :\overset{\ominus}{\text{CH}}_2\overset{\oplus}{\text{N}}{\equiv}\text{N} \;\rightarrow\; [\text{ArHgCH}_2\text{N}{\equiv}\text{N}]^{\oplus}[\text{RCOO}]^{\ominus}$$
$$\downarrow$$
$$\text{ArHgCH}_2\text{OOCR} \;+\; \text{N}_2$$
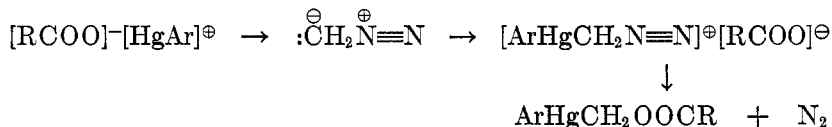
Huisgen (22), in his discussion of the reactions of aliphatic diazo compounds, postulates a similar mechanism which differs from the two above in that the initial addition complex is a zwitterion (IV) and that after loss of nitrogen the halomethyl compound is obtained by a 1,2-shift:

$$\text{HgCl}_2 \;+\; :\overset{\ominus}{\text{CH}}_2\overset{\oplus}{\text{N}}{\equiv}\text{N} \;\rightarrow\; \underset{\underset{\text{Cl}}{|}}{\text{Cl}\overset{\ominus}{\text{Hg}}\text{CH}_2\overset{\oplus}{\text{N}}{\equiv}\text{N}} \;\rightarrow\; \underset{\underset{\text{Cl}}{|}}{\text{Cl}\overset{\ominus}{\text{Hg}}\overset{\oplus}{\text{CH}}_2} \;\rightarrow\; \text{ClHgCH}_2\text{Cl}$$
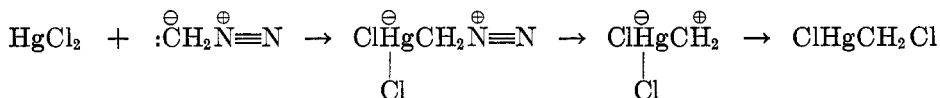
IV

The possibility that the initial addition, loss of nitrogen, and rearrangement to the halomethyl compound occur *via* a concerted process instead of stepwise must also be considered. It should be pointed out that the loss of nitrogen follows as a result of the loss of the resonance stabilization of the free diazomethane molecule in the primary addition product.

Yakubovich and Ginsburg (56), on the other hand, in their discussion of the methylenation of silicon halides have suggested a free-radical mechanism. The free methylene radical, it is claimed, is formed first,

$$\text{CH}_2\text{N}_2 \rightarrow :\text{CH}_2 + \text{N}_2$$
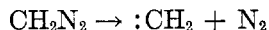
and is then said to "enter the location of the silicon–halogen bond" and to be thus prevented from entering into a polymerization reaction with the other free methylene radicals:

$$:\text{CH}_2 + \text{X}_3\text{SiX} \rightarrow \text{X}_3\text{SiCH}_2\text{X}$$

A consideration of the experimental evidence presented in the previous section, however, tends to favor the polar mechanism.

As has been pointed out (41), all metals whose halides undergo the methylenation reaction have available d-orbitals and thus a primary coördination step, as is suggested in the polar mechanism, is possible in all cases.

The reactions of organic halides with diazomethane provide an interesting example of how the availability of orbitals for coördination of the attacking diazomethane molecule determines the course of the reaction. Diazomethane reacts with acyl halides to give either halomethylketones (VII) or diazoketones (VI), depending on whether or not an excess of diazomethane is used. The course of the reaction has been formulated as follows:

$$\underset{\text{O}}{\overset{\text{O}}{\underset{\|}{R\overset{\|}{C}Cl}}} \;+\; :\overset{\ominus}{C}H_2\overset{\oplus}{N}\!\!\equiv\!\!N \;\rightarrow\; \begin{matrix} \overset{\ominus}{O} \\ | \\ R\overset{}{C}Cl \\ | \\ CH_2 \\ | \\ \overset{\oplus}{N}\!\!\equiv\!\!N \\ V \end{matrix}$$

$$\begin{matrix} \overset{\ominus}{O} \\ | \\ R\overset{}{C}Cl \\ | \\ CH_2 \\ | \\ \overset{\oplus}{N}\!\!\equiv\!\!N \end{matrix} \;\rightarrow\; \begin{matrix} \overset{\text{O}}{\overset{\|}{R C}}\!-\!\overset{\ominus}{\overset{\cdot\cdot}{C}}H\!-\!\overset{\oplus}{N}\!\!\equiv\!\!N \\ \updownarrow \\ \overset{\text{O}}{\overset{\|}{R\!-\!C}}\!-\!CH\!=\!\overset{\oplus}{N}\!=\!\overset{\ominus}{N} \\ VI \end{matrix} \;+\; HCl$$
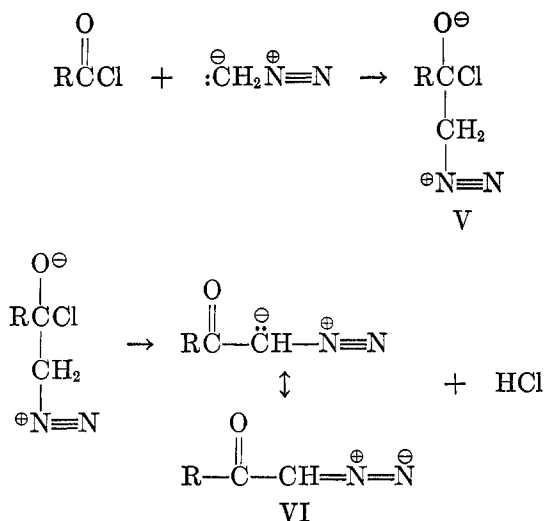
(*a*) If diazomethane is present in twofold excess:

$$CH_2N_2 + HCl \rightarrow CH_3Cl + N_2$$
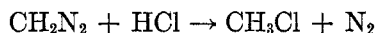
and the diazoketone is isolated.

(*b*) If equivalent amounts of diazomethane and the acyl halide are used:

$$\underset{}{\overset{\text{O}}{\overset{\|}{R\overset{}{C}}}CHN_2} \;+\; HCl \;\rightarrow\; \underset{VII}{\overset{\text{O}}{\overset{\|}{R\overset{}{C}}}CH_2Cl} \;+\; N_2$$
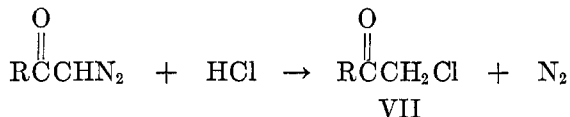
Here the reaction proceeds *via* a polar mechanism; nucleophilic attack of the diazomethane molecule gives an addition complex (V), which then decomposes to give the products.

On the other hand, polyhalomethanes cannot coördinate with the diazomethane molecule in the primary step, since the central carbon atom has no way of freeing an orbital by means of an electronic shift, nor does it have d-orbitals that are energetically capable of such a primary coördination. Polyhalomethanes must

then react by a free-radical mechanism. This has been shown to be the case (53). The reactions of diazomethane with polyhalomethanes, such as carbon tetrachloride and trichlorobromomethane, are light-induced, are inhibited by diphenylamine, are of zero order, and occur only with those halides which are known to undergo free-radical addition to olefins. When carbon tetrachloride is treated with diazomethane, *only* pentaerythrityl chloride, $C(CH_2Cl)_4$, is obtained, and the following course of reaction was suggested to explain this observation:

$$CH_2N_2 \rightarrow :CH_2 + N_2$$

$$:CH_2 + CCl_4 \rightarrow \cdot CH_2Cl + \cdot CCl_3$$

$$\cdot CCl_3 + CH_2N_2 \rightarrow N_2 + \cdot CH_2CCl_3$$

$$\cdot CH_2CCl_3 \rightarrow ClCH_2\overset{\cdot}{C}Cl_2$$

$$ClCH_2\overset{\cdot}{C}Cl_2 + CH_2N_2 \rightarrow ClCH_2\underset{\underset{\cdot CH_2}{|}}{C}Cl_2 + N_2$$

$$ClCH_2\underset{\underset{\cdot CH_2}{|}}{C}Cl_2 \rightarrow ClCH_2\underset{\underset{CH_2Cl}{|}}{\overset{\cdot}{C}}Cl$$

$$ClCH_2\underset{\underset{CH_2Cl}{|}}{\overset{\cdot}{C}}Cl + CH_2N_2 \rightarrow ClCH_2\underset{\underset{CH_2Cl}{|}}{\overset{\overset{\cdot CH_2}{|}}{C}}Cl + N_2$$

$$ClCH_2\underset{\underset{CH_2Cl}{|}}{\overset{\overset{\cdot CH_2}{|}}{C}}Cl \rightarrow (ClCH_2)_3C\cdot$$

$$(ClCH_2)_3C\cdot + CH_2N_2 \rightarrow (ClCH_2)_3CCH_2\cdot + N_2$$

$$(ClCH_2)_3CCH_2\cdot + CCl_4 \rightarrow (ClCH_2)_4C + \cdot CCl_3$$

The behavior of the acid halides of sulfur toward diazomethane (i.e., RSCl and RSOCl react, while RSO_2Cl does not), which at first sight appears inconsistent, can be explained when one considers Koch and Moffitt's treatment of the extent of d_π-p_π bonding in sulfones (25). As one goes up the series RSCl, RSOCl, and RSO_2Cl the d_π-p_π bonding between the sulfur and oxygen increases, and this double bonding may exert a blocking effect on the methylenation of sulfonyl halides.

Consideration of the yield data of methylenation reactions indicates that diethyl ether is the most favorable solvent for this reaction. In the case of tin halides better yields are obtained when the relatively polar solvent ether is used than when the reaction is carried out in benzene solution. This solvent dependence indicates the operation of a polar mechanism.

The yield data of the reaction of diazomethane with substituted chlorosilanes also favor a polar mechanism. Yields of methylenation product decrease in the

order $SiCl_4 > ClCH_2SiCl_3 > CH_3SiCl_3 \frown (ClCH_2)_2SiCl_2 > (CH_3)_2SiCl_2$, while trialkylchlorosilanes are not methylenated at all. It may be seen from this series that electronegative substituents on the silicon atom apparently favor the methylenation reaction. That electron-withdrawing groups accelerate the nucleophilic reactions of diazomethane has been observed in the reaction of diazomethane with ketones (20). Thus, acetone itself is unreactive toward ethereal diazomethane, but negatively substituted acetones, such as chloroacetone, trichloroacetone, and methoxyacetone, react under these conditions. If the steric factor alone were important, one would expect that methyltrichlorosilane would be more readily methylenated than chloromethyltrichlorosilane and bis-(chloromethyl)dichlorosilane. Evidence for these electronic effects provides further indication that the methylenation reaction proceeds *via* the polar mechanism. It seems likely that in the case of triethylchlorosilane and triphenylchlorosilane electronic and steric effects are equally important. Yakubovich's argument (56) for the free-radical mechanism based on the fact that the reactivity decrease $RSiCl_3 > R_2SiCl_2 > R_3SiCl$ for the methylenation reaction parallels that of the hydrolysis of the alkylchlorosilanes is not valid, since it is known that the hydrolysis reaction proceeds *via* a polar mechanism that involves primary coördination of the nucleophilic hydroxide ion or water molecule to the silicon atom (36).

A similar series cannot be written for the tin halides, since some of the methylenations were carried out in benzene solution and others in ether. However, it may be pointed out that it is possible to prepare tetrakis(halomethyl)tin compounds, but that unsubstituted triorganotin halides do not react with diazomethane. Even when dimethyltin dichloride was treated with an excess of diazomethane, only chloromethyldimethyltin chloride was obtained. It thus seems likely that the same electronic effects are operative in the methylenation of tin halides.

In the case of tin halides the ease of reaction as the halogen atom is varied seems to decrease as follows:

$$Sn—I > Sn—Br > Sn—Cl; \qquad Sn—F \text{ does not react}$$
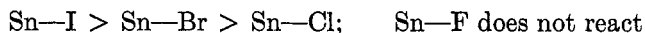
This dependence on the halogen, and hence on the nature of the tin–halogen bond, can be interpreted to favor either the polar or the free-radical mechanism, since this series represents (*a*) the decrease in the ease of ionization of the Sn—X bond (for polar mechanism) and (*b*) the increase in the Sn—X bond energies (for free-radical mechanism).

The anomalous behavior of ethyl diazoacetate toward tin tetrachloride may be explained by the participation of another resonance form in which the carbonyl oxygen atom bears the negative charge:

VIIIa   VIIIb
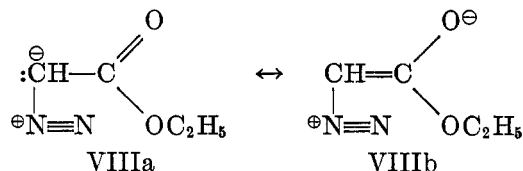
Form VIIIb then is the most important, and a product with tin–oxygen bonds is obtained. A product with iron–oxygen bonds is similarly obtained when ferric chloride is treated with ethyl diazoacetate (30).

The boron halides are the only halides of the B subgroup metals that yield no halomethyl derivatives on treatment with diazomethane in ether. Only decomposition of the diazomethane and polymerization to a polymethylene of very high molecular weight occurred in all cases. This unique behavior is undoubtedly related to the presence of the empty p-orbitals in the boron halides and their resultant strong Lewis acid properties. Consideration of the polar nature of the ether used as solvent and the tendency of boron trifluoride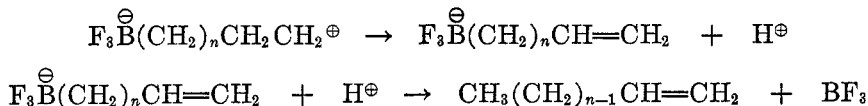 to enter into polar-type reactions led Kantor and Osthoff (24) to propose the following mechanism for the boron trifluoride-catalyzed decomposition of diazomethane:

$$BF_3 \ + \ :\overset{\ominus}{C}H_2\overset{\oplus}{N}\!\!\equiv\!\!N \ \rightarrow \ F_3\overset{\ominus}{B}CH_2\overset{\oplus}{N}\!\!\equiv\!\!N$$

$$F_3\overset{\ominus}{B}CH_2\overset{\oplus}{N}\!\!\equiv\!\!N \ \rightarrow \ F_3\overset{\ominus}{B}CH_2{}^{\oplus} \ + \ N_2$$

$$F_3\overset{\ominus}{B}CH_2{}^{\oplus} \ + \ CH_2N_2 \ \rightarrow \ F_3\overset{\ominus}{B}CH_2CH_2\overset{\oplus}{N}\!\!\equiv\!\!N$$

$$F_3\overset{\ominus}{B}CH_2CH_2\overset{\oplus}{N}\!\!\equiv\!\!N \ \rightarrow \ F_3\overset{\ominus}{B}CH_2CH_2{}^{\oplus} \ + \ N_2$$
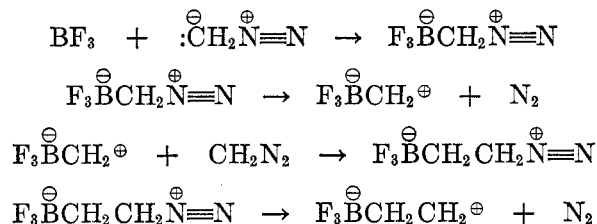
etc., until termination occurs:

$$F_3\overset{\ominus}{B}(CH_2)_nCH_2CH_2{}^{\oplus} \ \rightarrow \ F_3\overset{\ominus}{B}(CH_2)_nCH\!\!=\!\!CH_2 \ + \ H^{\oplus}$$

$$F_3\overset{\ominus}{B}(CH_2)_nCH\!\!=\!\!CH_2 \ + \ H^{\oplus} \ \rightarrow \ CH_3(CH_2)_{n-1}CH\!\!=\!\!CH_2 \ + \ BF_3$$

This proposed mechanism finds support from the previous observation of Meerwein (27) that the effectiveness of the alkyl borates in the catalysis of the decomposition of diazomethane increases with their ability to form complexes, as determined by their tendency to coördinate alkali alcoholates. A subsequent detailed kinetic study of the boron trifluoride-catalyzed decomposition of diazomethane by Bawn and Rhodes (6) has made it necessary to write the termination step:

$$F_3\overset{\ominus}{B}(CH_2)_nCH_2{}^{\oplus} \ + \ :\overset{\ominus}{C}H_2\overset{\oplus}{N}\!\!\equiv\!\!N \ \rightarrow \ \text{dead polymer}$$
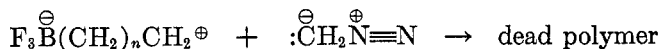
i.e., monomer deactivation, in order to obtain agreement with the experimentally observed kinetic expression. Bawn and Rhodes state further that, since the polymers they obtained contained about 1.2 per cent nitrogen, the possibility that the initiation occurs *via* boron–nitrogen coördination:

$$\overset{\oplus}{C}H_2N\!\!=\!\!\overset{\ominus}{N} \ + \ BF_3 \ \rightarrow \ \overset{\oplus}{C}H_2N\!\!=\!\!N\overset{\ominus}{B}F_3$$
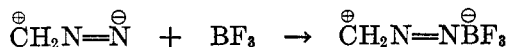
and that the polymerization continues

$$\overset{\oplus}{C}H_2N\!\!=\!\!\overset{\ominus}{N} \ + \ \overset{\oplus}{C}H_2N\!\!=\!\!N\overset{\ominus}{B}F_3 \ \rightarrow \ N\!\!\equiv\!\!\overset{\oplus}{N}(CH_2)_2N\!\!=\!\!N\overset{\ominus}{B}F_3$$

$$N\!\!\equiv\!\!\overset{\oplus}{N}(CH_2)_nN\!\!=\!\!N\overset{\ominus}{B}F_3 \ \rightarrow \ N_2 \ + \ \overset{\oplus}{C}H_2(CH_2)_{n-1}N\!\!=\!\!N\overset{\ominus}{B}F_3$$
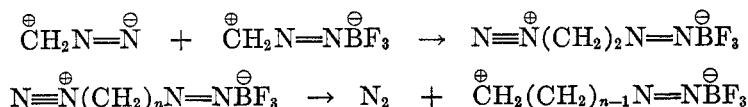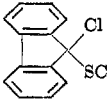
TABLE 1

Methylenation products

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
$ClCH_2HgCl$	131				(21)
$Hg(CH_2Cl)_2$	37–40				(21)
$C_6H_5CH_2HgCl$		Oil			(21)
$Hg(CH_2I)_2$	82–84				(21)
$(C_3H_5)_2CClHgCl$		Pale yellow solid			(21)
$BrCH_2HgBr$	124.5–125.5				(19)
$Hg(CH_2Br)_2$	42–43				(19)
$Hg[C(Cl)(HgCl)COOC_2H_5]_2$	Does not melt				(29)
$C_6H_5HgCH_2OCOC_6H_5$	80				(32)
$C_6H_5HgCH_2OCOC_6H_4OH\text{-}o$	106				(32)
$C_6H_5HgCH_2OCOC_6H_4OCH_3\text{-}o$	76				(32)
$p\text{-}CH_3C_6H_4HgCH_2OCOC_6H_5$	82				(33)
$p\text{-}CH_3C_6H_4HgCH_2OCOC_6H_4OH\text{-}o$ ...	104				(33)
$p\text{-}CH_3C_6H_4HgCH_2OCOC_6H_4Cl\text{-}p$	97–99				(33)
$\alpha\text{-}C_{10}H_7HgCH_2OCOC_6H_5$	78				(33)
$\alpha\text{-}C_{10}H_7HgCH_2OCOC_6H_4OH\text{-}o$	126				(33)
$\alpha\text{-}C_{10}H_7HgCH_2OCOC_6H_4NO_2\text{-}p$	136				(33)
$\beta\text{-}C_{10}H_7HgCH_2OCOC_6H_5$	91				(33)
$\beta\text{-}C_{10}H_7HgCH_2OCOC_6H_4OH\text{-}o$	85				(33)
$p\text{-}C_6H_5C_6H_4HgCH_2OCOC_6H_5$	96				(33)
$p\text{-}C_6H_5C_6H_4HgCH_2OCOC_6H_4OH\text{-}o$ ..	118				(33)
$p\text{-}C_6H_5C_6H_4HgCH_2OCOC_6H_4NO_2\text{-}p$.	112				(33)
$(ClCH_2)_2TlCl$					(54)
$[(CH_3CHCl)TlCl]_2O$					(54)
$ClCH_2SiCl_3$		116.5/750 mm.	1.4450[a]	1.4776[e]	(56, 42)
		111–112/769 mm.			
$ClCH_2SiHCl_2$		97–97.5/773 mm.			(42)
$(ClCH_2)_2SiCl_2$		58.5/16 mm.		1.4624[e]	(56)
$(ClCH_2)_3SiCl$		70/4 mm.		1.4377[e]	(56)
$CH_3(CH_2Cl)SiCl_2$		121–122		1.2778[e]	(56)
$CH_3CHClSiCl_3$		66/75 mm.		1.3919[e]	(56)
$BrCH_2SiBr_3$		70/6 mm.		2.5730[e]	(56)
$(BrCH_2)_2SiBr_2$		107/9 mm.		2.4614[e]	(56)
$(BrCH_2)_3SiBr$		122–123/5 mm.		2.3440[e]	(56)
$ClCH_2GeCl_3$		60–65/35 mm.	1.4989[b]	1.833[d]	(42)
$(ClCH_2)_2GeCl_2$		90/21 mm.	1.5176[b]		(42)
$CH_3(CH_2Cl)GeCl_2$		71–74/40 mm.	1.4890[b]	1.642[d]	(42)
$CH_3(CH_2Cl)_2GeCl$		95–97/30 mm.	1.5010[b]		(42)
$ClCH_2SnCl_3$		72.5–73/5 mm.	1.5689[a]	2.21[e]	(59)
$(ClCH_2)_2SnCl_2$	89.5–90				(59)
$(ClCH_2)_3SnCl$		138–140/5 mm.	1.593[a]	2.03[e]	(59)
$(ClCH_2)_4Sn$	49–49.5	148.5/5 mm.			(59)
$BrCH_2SnBr_3$		109/5 mm.		3.251[e]	(59)
$(BrCH_2)_2SnBr_2$	87	155–160/5 mm.			(59)
$(BrCH_2)_3SnBr$					(59)
$(BrCH_2)_4Sn$	57				(59)
$(CH_3CHCl)_2SnCl_2$	12	112/4 mm.	1.5535[a]	1.829[e]	(59)
$(CH_3CHCl)_3SnCl$		130/3 mm.	1.5450[a]	1.684[e]	(59)
$(CH_3CHCl)_4Sn$		142/2 mm.	1.5365[a]	1.568[e]	(59)
$(C_3H_7CHCl)_2SnCl_2$	53	134/5 mm.			(59)
$(ClCH_2)(CH_3CHCl)_3SnCl$		128/3 mm.	1.555[a]	1.765[e]	(43)
$(ClCH_2)_2(CH_3CHCl)_2Sn$		141–142/5 mm.	1.578[a]	1.675[e]	(43)
$(CH_3)_2(CH_2Cl)SnCl$		76–77/11 mm.	1.5263[b]		(43)
$(CH_3)_2(CH_2Br)SnBr$		75–79/3.5–4 mm.	1.5683[b]		(43)
$(CH_3)_2(CH_2I)SnI$		111–111.2/5 mm.	1.6690[b]		(43)

TABLE 1—*Concluded*

Compound	Melting Point	Boiling Point	n_D	d	References
	°C.	°C.			
$(n\text{-}C_4H_9)_2(CH_2Cl)SnCl$		106–110/0.3 mm.	$1.5095^{(b)}$	$1.378^{(d)}$	(43)
$n\text{-}C_4H_9(CH_2Cl)_2SnCl$		82–87/0.18–0.2 mm.	$1.5394^{(b)}$	$1.649^{(d)}$	(43)
$(C_6H_5)_2(CH_2Br)SnF$	>260				(43)
$(C_2H_5)_3(CH_2Cl)Pb$		65.5–66.5/3 mm.	$1.5434^{(a)}$	$1.7917^{(c)}$	(61)
$(C_2H_5)_2(CH_2Cl)_2Pb$		96/2 mm.		$1.9890^{(c)}$	(61)
$ClCH_2NO_2$		122–123/atmospheric pressure			(52)
$O_2NCH(Cl)COOC_2H_5$		88/0.04 mm.			(52)
$ClCH_2PCl_2$		77–78/140 mm.	$1.5247^{(a)}$	$1.5289^{(e)}$	(55)
$CH_3CHClPCl_2$		61.5–62.5/50 mm.	$1.5090^{(a)}$	$1.4232^{(e)}$	(55)
$C_3H_7CHClPOCl_2$		84/25 mm.	$1.5010^{(a)}$	$1.3236^{(e)}$	(55)
$BrCH_2PBr_2$		70/4 mm.		$2.6357^{(e)}$	(55)
$(ClCH_2)_3PO$	100.5				(55)
$(CH_3CHCl)_2P(O)OH$	107				(55)
$(sec\text{-}C_4H_9O)_2P(O)CH_2F$		96–100/3 mm.			(37)
$ClCH_2AsCl_2$		57–58/16 mm.		$1.9806^{(g)}$	(8)
$(ClCH_2)_2AsCl$		86–88/16 mm.		$1.8485^{(h)}$	(8)
$(CH_3CHCl)_2AsCl$		51.5/1 mm. 61–61.5/3 mm.	$1.5370^{(f)}$	$1.553^{(e)}$	(58)
$(CH_3CHCl)_3As$		69.5–70.2/1 mm. 81–82/2 mm.	$1.5307^{(e)}$	$1.445^{(e)}$	(58)
$(C_6H_5)_2As(O)CH_2As(C_6H_5)_2$	184–186				(14)
$ClCH_2SbCl_2$	36–38	86.5/2 mm. 91–98/7 mm.		$2.677^{(e)}$	(58)
$(ClCH_2)_3Sb$	90–90.5				(58)
$(CH_3CHCl)_2SbCl$		88–88.5/3 mm. 69.5/1 mm.		$1.831^{(e)}$	(58)
$ClCH_2BiO$					(58)
$(C_6H_5)_2C(Cl)SC_6H_4NO_2\text{-}o$	Decomposes at 137				(38)
![structure] $SC_6H_4NO_2\text{-}o$	Decomposes at ~120				(38)
$(C_6H_5)_2C(Cl)SC_6H_5$	Isolated as $(C_6H_5)_2C(SC_6H_5)SC_6H_4NO_2\text{-}o$				(38)
$o\text{-}O_2NC_6H_4SCH_2Cl$	95				(39)
$(C_6H_5)_2C(Br)SC_6H_4NO_2\text{-}o$	108				(39)
$(C_6H_5)_2C(Cl)SC_6H_3(Cl\text{-}p)(NO_2\text{-}o)$	121				(39)
$(ClCH_2)_2SO$	39	55/0.7 mm.			(37)

(a) $n_D^{20°}$. (b) $n_D^{25°}$. (c) $d_4^{20°}$. (d) $d_4^{25°}$. (e) $d_{20°}^{20°}$. (f) $n_D^{21.5°}$. (g) $d_{15°}^{17°}$. (h) $d_{15°}^{20°}$.

and ends by monomer termination

$$N\!\!\equiv\!\!\overset{\oplus}{N}(CH_2)_n\overset{\ominus}{B}F_3 \;+\; \overset{\oplus}{C}H_2N\!\!=\!\!\overset{\ominus}{N} \;\rightarrow\; N\!\!\equiv\!\!\overset{\oplus}{N}(CH_2)_nN\!\!=\!\!\overset{\ominus}{N} \;+\; \overset{\oplus}{C}H_2N\!\!=\!\!\overset{\ominus}{N}BF_3$$
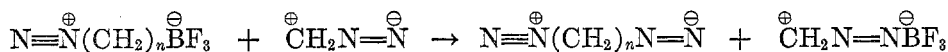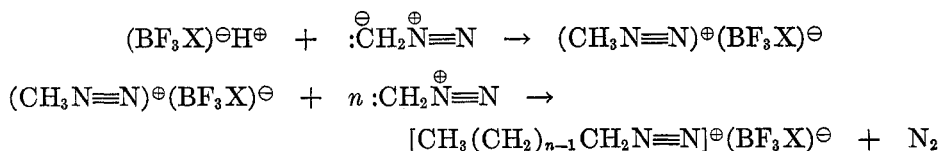
is a strong one. However, it should be pointed out that these are the only investigators whose polymethylene had such a relatively high nitrogen content.

Other workers (18) have studied the kinetics of this reaction and have agreed

that an ionic mechanism operates. Free-radical inhibitors had no effect on the decomposition of diazomethane by boron trifluoride. However, these investigators believe that the boron trifluoride is complexed with a cocatalyst (water, methanol, ethyl ether) as $[BF_3X]^{\ominus}H^{\oplus}$ and that the reaction steps then are:

$$(BF_3X)^{\ominus}H^{\oplus} \;+\; :\overset{\ominus}{C}H_2\overset{\oplus}{N}\!\!\equiv\!\!N \;\rightarrow\; (CH_3N\!\!\equiv\!\!N)^{\oplus}(BF_3X)^{\ominus}$$

$$(CH_3N\!\!\equiv\!\!N)^{\oplus}(BF_3X)^{\ominus} \;+\; n\;:CH_2\overset{\oplus}{N}\!\!\equiv\!\!N \;\rightarrow$$

$$[CH_3(CH_2)_{n-1}CH_2N\!\!\equiv\!\!N]^{\oplus}(BF_3X)^{\ominus} \;+\; N_2$$

with termination occurring through a transfer reaction.

IV. METHYLENATION PRODUCTS

Table 1 presents a summary of the organometallic and organometalloidal compounds which have been prepared by the methylenation reactions described in this review.[2]

The author is indebted to Professor Eugene G. Rochow for his interest and encouragement and to Professor R. Huisgen for valuable discussions relating to the section on the mechanism of the methylenation reaction.

V. REFERENCES

(1) ARNDT, F. G.: Angew. Chem. **40**, 1099 (1927).
(2) ARNDT, F. G.: Angew. Chem. **64**, 592 (1952).
(3) ARNDT, F. G.: In *Organic Analysis*, Vol. I, pp. 197–242. Interscience Publishers, Inc., New York (1953).
(4) ARNDT, F. G., AND SCHOLZ, H.: Ber. **66**, 1012 (1933).
(5) BACHMANN, W. E., AND STRUVE, W. S.: Org. Reactions **1**, 50 (1942).
(6) BAWN, C. E. H., AND RHODES, T. B.: Trans. Faraday Soc. **50**, 934 (1954).
(7) BOERSCH, H.: Monatsh. **65**, 331 (1935).
(8) BRAZ, G. I., AND YAKUBOVICH, A. Ya.: J. Gen. Chem. (U.S.S.R.) **11**, 41 (1941); Chem. Abstracts **35**, 5459 (1941).
(9) BUCHNER, E.: Ber. **28**, 218 (1895).
(10) BUCKLEY, G. D., AND RAY, N. H.: J. Chem. Soc. **1952**, 3701.
(11) CARONNA, G., AND SANSONE, S.: Atti X° congr. intern. chim. **3**, 77 (1939); Chem. Abstracts **34**, 980 (1940).
(12) CLIBBENS, D. A., AND NIERENSTEIN, M.: J. Chem. Soc. **107**, 1491 (1915).
(13) COLEMAN, G. H., GILMAN, H., ADAMS, C. E., AND PRATT, P. E.: J. Org. Chem. **3**, 99 (1938).
(14) COOKSON, G. H., AND MANN, F. G.: J. Chem. Soc. **1949**, 2895.
(15) CRAWFORD, B. L., FLETCHER, W. H., AND RAMSAY, D. A.: J. Chem. Phys. **19**, 406 (1951).
(16) DILLARD, C. R.: Final Report, O.N.R. Contract N9-onr-95700, August 31, 1952.
(17) EISTERT, B.: Angew. Chem. **54**, 99, 124 (1941); translated and revised by Spangler in

[2] Since this manuscript was submitted the first chloromethyl derivative of a transition metal, $C_5H_5Cr(NO)_2CH_2Cl$, green crystals melting at 71°C., has been prepared in 4 per cent yield by treatment of $C_5H_5Cr(NO)_2Cl$ with diazomethane (1:3 molar ratio) at room temperature in the presence of copper powder (T. S. Piper and G. Wilkinson: Private communication; Chemistry & Industry **1955**, 1296).

Newer Methods of Preparative Organic Chemistry, 1st edition, pp. 513–70, Interscience Publishers, Inc., New York (1948).

(18) FELTZIN, J., RESTAINO, A. J., AND MESROBIAN, R. B.: J. Am. Chem. Soc. **77**, 206 (1955).

(19) FREIDLINA, R. K., NESMEYANOV, A. N., AND TOKAREVA, F. A.: Ber. **69B**, 2019 (1936).

(20) GUTSCHE, C. D.: Org. Reactions **8**, 364 (1954).

(21) HELLERMAN, L., AND NEWMAN, M.D.: J. Am. Chem. Soc. **54**, 2859 (1932).

(22) HUISGEN, R.: Österr. Chem. Ztg. **55**, 237 (1954).

(23) HURD, C. D.: In Gilman's *Organic Chemistry*, 1st edition, Vol. I, pp. 645–56. John Wiley and Sons, Inc., New York (1938).

(24) KANTOR, S. W., AND OSTHOFF, R. C.: J. Am. Chem. Soc. **75**, 931 (1953).

(25) KOCH, H. P., AND MOFFITT, W.: Trans. Faraday Soc. **47**, 7 (1951).

(26) KRAUSE, E., AND GROSSE, A. VON: *Die Chemie der metallorganischen Verbindungen*, pp. 335–53. Gebrüder Bornträger, Berlin (1937).

(27) MEERWEIN, H.: Angew. Chem. **60**, 78 (1948).

(28) MEERWEIN, H., AND HINZ, G.: Ann. **484**, 11 (1930).

(29) NESMEYANOV, A. N., AND POVCH, G. S.: Ber. **67B**, 971 (1934).

(30) NESMEYANOV, A. N., AND SEGALEVICH, A. E.: Bull. acad. sci. U.R.S.S., Classe sci. chim. **1942**, 8; Chem. Abstracts **37**, 3055 (1943).

(31) PECHMANN, H. VON: Ber. **27**, 1888 (1894).

(32) PFEIFFER, P., AND JÄGER, H.: Chem. Ber. **80**, 1 (1947).

(33) PFEIFFER, P., SCHULZE-BENTROP, R., LA ROCHE, K. H., AND SCHMITZ, E.: Chem. Ber. **85**, 232 (1952).

(34) PLETZ, W. M.: J. Gen. Chem. (U.S.S.R.) **7**, 270 (1937); Chem. Zentr. **1938**, II, 4595.

(35) RAMSAY, D. A.: J. Chem. Phys. **17**, 666 (1949).

(36) ROCHOW, E. G.: *An Introduction to the Chemistry of the Silicones*, 2nd edition, pp. 22–3. John Wiley and Sons, Inc., New York (1951).

(37) SAUNDERS, B. C., AND STACEY, G. J.: J. Chem. Soc. **1948**, 702.

(38) SCHÖNBERG, A., SCHÜTZ, O., AND PETER, J.: Ber. **62**, 1663 (1929).

(39) SCHÖNBERG, A., AND STOLPP, T.: Ber. **63**, 3102 (1930).

(40) SCHROEDER, W., AND KATZ, L.: J. Org. Chem. **19**, 718 (1954).

(41) SEYFERTH, D.: Ph.D. Thesis, Harvard University, 1954.

(42) SEYFERTH, D., AND ROCHOW, E. G.: J. Am. Chem. Soc. **77**, 907 (1955).

(43) SEYFERTH, D., AND ROCHOW, E. G.: J. Am. Chem. Soc. **77**, 1302 (1955).

(44) SIDGWICK, N. V.: *The Organic Chemistry of Nitrogen*, new edition, revised and rewritten by T. W. J. Taylor and W. Baker, pp. 347–63. Oxford University Press, London (1942).

(45) SKINNER, G. S.: J. Am. Chem. Soc. **46**, 731 (1924).

(46) SMITH, L. I.: Chem. Revs. **23**, 193 (1938).

(47) STAUDINGER, H.: Chem. Ztg. **1914**, 758.

(48) STAUDINGER, H., ANTHES, E., AND PFENNINGER, F.: Ber. **49**, 1928 (1916).

(49) STAUDINGER, H., AND GAULE, A.: Ber. **49**, 1951 (1916).

(50) STAUDINGER, H., AND MÄCHLING, C.: Ber. **49**, 1973 (1916).

(51) STAUDINGER, H., AND MEYER, J.: Helv. Chim. Acta **2**, 619 (1919).

(52) STEINKOPF, W., AND KÜHNEL, M.: Ber. **75B**, 1323 (1942).

(53) URRY, W. H., AND EISZNER, J. R.: J. Am. Chem. Soc. **74**, 5822 (1952).

(54) YAKUBOVICH, A.YA., AND GINSBURG, V. A.: Doklady Akad. Nauk S.S.S.R. **73**, 957 (1950); Chem. Abstracts **45**, 2857 (1951).

(55) YAKUBOVICH, A. YA., AND GINSBURG, V. A.: J. Gen. Chem. (U.S.S.R.) **22**, 1534 (1952); Chem. Abstracts **47**, 9254 (1953).

(56) YAKUBOVICH, A. YA., AND GINSBURG, V. A.: J. Gen. Chem. (U.S.S.R.) **22**, 1783 (1952); Chem. Abstracts **47**, 9256 (1953).

(57) YAKUBOVICH, A. YA., GINSBURG, V. A., AND MAKAROV, S. P.: Doklady Akad. Nauk S.S.S.R. **71**, 303 (1950); Chem. Abstracts **44**, 8320 (1950).

(58) YAKUBOVICH, A. YA., AND MAKAROV, S. P.: J. Gen. Chem. (U.S.S.R.) **22,** 1528 (1952); Chem. Abstracts **47,** 8010 (1953).

(59) YAKUBOVICH, A. YA., MAKAROV, S. P., AND GAVRILOV, G. I.: J. Gen. Chem. (U.S.S.R.) **22,** 1788 (1952); Chem. Abstracts **47,** 9257 (1953).

(60) YAKUBOVICH, A. YA., MAKAROV, S. P., GINSBURG, V. A., GAVRILOV, G. I., AND MERKULOVA, J. N.: Doklady Akad. Nauk S.S.S.R. **72,** 69 (1950); Chem. Abstracts **45,** 2856 (1951).

(61) YAKUBOVICH, A. YA., MERKULOVA, J. N., MAKAROV, S. P., AND GAVRILOV, G. I.: J. Gen. Chem. (U.S.S.R.) **22,** 2060 (1952); Chem. Abstracts **47,** 9257 (1953).

(62) ZERNER, E.: Monatsh. **34,** 1609, 1631 (1914).